

## II. The Second Law in Relation to Thermal Radiative Transfer

Christopher G. Jesudason

*Chemistry Department and Center for Theoretical and Computational Physics  
University of Malaya, 50603 Kuala Lumpur, Malaysia*

**Abstract.** Planck introduced the quantum hypothesis from his Blackbody radiation studies, where he and subsequent workers opined that classical mechanics and electrodynamical theories could not account for the phenomenon. Hence a statistical mechanics with an appropriate Second law entropy was invented and coupled to the First law to account for quantum effects. Here, as an academic exercise we derive the quantum of energy by considering two structures, that of the dipole oscillators on a 2-D surface and the scattering of radiation into the 3-D cavity. Previous derivations are briefly cited and reviewed where none followed this approach. One prediction from this first order Brownian motion development is that a 2-D sheet of oscillators should emit radiation largely with energy density factor  $T^1$  of the Kelvin temperature  $T$ , rather than that deduced as  $T^4$  from detailed balance. Preliminary measurements conducted here seemed to verify the  $T^1$  density. The first order theory also admits a possibility of nonlinear quanta and the consequences are explored briefly. It was noticed in passing during the experimentation that certain bodies suspended in a vacuum exhibited small persistent temperature differentials. A Second law statement is presented for such cases and consequences explored for processes that are not coupled by Newtonian momentum energy transfer mechanisms, such as for the radiation field as deduced by Planck. The different forms of heat transfer due to different laws (e.g. gravity waves and electromagnetic waves) are strictly separable and cannot be confused or forced to an equivalence. We generalize on the Zeroth law, the Kirchhoff law and postulate an appropriate entropy form due to these generalizations.

**Keywords:** Planck and Kirchhoff Radiation laws, Entropy, Equilibrium temperature differentials, Generalized Second Law

**PACS:** 05.70.-a, 05.70.Np, 68.35.Md

### INTRODUCTION AND BACKGROUND

The background to this presentation was a work that derived the Blackbody (BB or bb) spectrum and Planck quanta from strictly classical arguments and first order Brownian motion theory which could distinguish the processes of the 2 - D surface of the BB cavity from the 3-D electromagnetic (*em*) cavity modes that builds up as a result of the surface scattering [1]. It also commented in detail contemporary developments that claimed from their titles to derive the Planck BB radiation law on classical grounds, where it was demonstrated in each case that this was not the case [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. [1] assumes the Zeroth law and thermal equilibrium of the surface oscillators and ergodicity [14, p.46] so that the density of probability  $w(X)$  is dependent on the energy of the system i.e.  $w(X) = \phi(H(X))$  where  $X$  are the canonical coordinates for a single system in an ensemble all having Hamiltonian  $H$ , also written  $H(X, a)$  with  $a$  being external or system variables; each  $a$  coordinate represents an entirely different Hamiltonian and all the results in classical statistical mechanics presumes that the statistical mechanical



ensemble is not mixed but is composed of similar systems with the same  $a$  variable. The equipartition results also assumes the same  $a$  values for all systems. It is maintained here that earlier work assumed different  $a$  values implying a mixed system that made them conclude that there was a failure in the results of statistical mechanics. The failure of their derivation was thought to lie in the breakdown of the equipartition theorem [15, pp.185-6] and where the inadequacy of mechanics is strongly maintained [15, pp. 117,189]. Jeans echoes similar sentiments [8, p.948] as does McLaren [12, pp.21,26]. A more recent critique of Jeans and Einstein is given in a pedagogical article [16]. These opinions probably helped drive the development of molecular orbital theory by assuming that classical electrodynamics represented average quantities that need not represent reality at the atomic level. What is attempted here is a completely classical derivation which Planck and his contemporaries thought impossible, and which is entirely different from the more current methods already alluded to. Planck invented a statistical mechanics that could overcome the equipartition principle [15, Part III, Entropy and Probability] for the Second law expression, whilst maintaining the First law without modification. The two laws of thermodynamics "must be upheld under all circumstances" [17, Planck, M. (1931). Letter to R.W. Wood,] according to Planck because the failure of equipartition [15, p.114] implied that the laws of (*Hamiltonian*) mechanics failed at the molecular level, and "a purely electro-dynamical theory fails entirely" [15, p.114]. The inadequacy of mechanics is strongly maintained by Planck [15, p.117,p.189, Sec. 170]. The approximate development below shows that no immediate and necessary modification is implied. On the other hand, preliminary experiments seem to support some of our predictions, and these with other possible predictions are presented in the next section. Here we develop a statistical mechanics for mixed systems with different  $a$  variables. The density  $w(X)$  [14, p.54, eqn. 11.27] for *identical* systems with the same  $a$  is given by

$$w(H) = \exp(\Psi(\Theta, a) - H(X, a)/\Theta) \quad (1)$$

and so the equipartition results for the  $\{p_k, q_k\}$  momentum-spatial coordinate set ,

$$\overline{p_k \partial H / \partial p_k} = \Theta \quad (2)$$

$$\overline{q_k \partial H / \partial q_k} = \Theta \quad (3)$$

which are based on (1), must refer to similar systems and to identical  $\Psi, a$  and  $\Theta$ , the temperature factor, where  $\Psi$  is the modulus, equivalent to the normalization constant. If *canonical* coordinates are involved [18], as they must as we are considering different oscillators, then from equipartition and (1) we have

$$w_{12}(X_1, X_2) = w_1(X_1) \cdot w_2(X_2) \quad (4)$$

where

$$w_i(X_i) = D_i \exp(-\beta H_i) \quad (5)$$

where the systems need *not* be identical but identical ones have one particular subscript  $j$  and belong to a particular energy channel;  $D_i$  need not all be identical although the temperature is (from the Zeroth law) for purely equilibrium mechanical systems. In our case, each elementary oscillator with a unique characteristic frequency is a different Hamiltonian system with a distinct  $a$  value so that the total system  $\Sigma$  is made up of composite



systems  $\Sigma_1, \Sigma_2 \dots \Sigma_n$  with different Hamiltonian structures in thermodynamical equilibrium where  $\Sigma = \Sigma_1 \cup \Sigma_2 \cup \Sigma_3 \dots \cup \Sigma_n$  would obey, for two canonical variables (in this case represented by the frequencies  $\omega$ ) would obey (4) so that the probability densities  $P \equiv w$  can be written  $P(\omega_i, \omega_j) = P_i(\omega_i)P_j(\omega_j)$  where the probability for each channel is  $w_i(\omega_i) = \exp(\Psi_i(\Theta, \omega_i) - H_i(\omega_i, a_i)/\Theta)$ . Henceforth,  $X$  will denote the *amplitude* of the various oscillators. These oscillators can be envisaged as the free electrons oscillating about the lattice cores of opposite charge where the mean distance between the particle and cores  $\langle X \rangle$  at high enough temperatures would be bounded and also slowly varying once the mean kinetic energy exceeds the mean potential energy; these oscillators vibrate at different frequencies with damped (combined electromagnetic and mechanical) average viscosity coefficient  $\gamma$  and breakup with mean relaxation time  $\tau$ . Since these two quantities pertain to the entire system, they can be used to coordinate the various processes. The radiation from these oscillators before breaking up are assumed to scatter into the stable modes of electromagnetic stationary waves within the cavity, where each mode is considered to be a different canonical system  $\Sigma_i$  in thermal equilibrium with the entire system  $\Sigma$ . The following is a deliberately simplified treatment to highlight the general approach; the theories of stochastic processes using the Itô and other integrations is sufficiently advanced to derive quantities to any degree of accuracy based on a model; here we concentrate on a feasible model and defer detailed treatment until the nature of the model is further clarified and understood. Clothing inappropriate models with mathematical abstractions can be a costly detour.

### Structure of the oscillator equations

After a particular oscillator configuration has been reached, it radiates without being forcefully driven. For any one amplitude  $X_0$ , the damped harmonic equation is

$$m\ddot{X} + a\dot{X} + kX = 0 \quad (6)$$

where  $a = \gamma m$ . The radiation within the cavity and particles on the surface cavity interacts to reconfigure the oscillator after time  $\tau$ . The damping is assumed small so that within this time frame of the relaxation time  $\tau_i$  for this oscillator characteristic, the trial solution for amplitude  $X_0$  is  $X = X_0 \exp(i\omega t)$  with natural frequency of vibration  $\omega^2 = k/m$ , with  $k$  the elastic constant and  $m$  the mass of the oscillator. Averaging over one period, the non-thermal coarse-averaged quantity for kinetic energy  $K'$ , potential energy  $V'$  and total energy  $E'$  has been worked out [19, Chap.23] as

$$K' = mX_0^2\omega^2/4 \quad (7)$$

$$V' = kX_0^2/4 \quad (8)$$

$$E' = mX_0^2\omega^2/2 \quad (9)$$

and from the above we infer that the average square amplitude  $\langle X_0^2 \rangle$  for this oscillator is such that the Kinetic  $K$ , Potential  $V$  and total energy  $E$  must preserve the above form so that  $K = m \langle X_0^2 \rangle \omega^2/4$ ,  $V = k \langle X_0^2 \rangle /4$ , and  $E = m \langle X_0^2 \rangle \omega^2/2$ . One

approximation we make here is that because we are working at high temperatures and because we are parameterizing the system over an average system relaxation time  $\tau$ , we shall also refer to  $X_0$  as pertaining to the average oscillator amplitude as well. Define the density of states  $\Gamma(E, a)$  such that

$$\Gamma(E, a) = \int_{H(X, a) < E} dX$$

where again  $X$  are the canonical coordinates. Then the entropy  $S$  is defined as  $S = k \ln \Gamma$  and from the definition of  $\Gamma$  and assumption of isotropy, it follows that  $\Gamma = \alpha E$  and from the definition (1) of the probability density of form  $P(E) = c \Omega(E) \exp -E\beta$  where  $\Theta = k_b T = 1/\beta$  and the identity  $1/T = \partial S / \partial E$  we can derive

$$\langle E \rangle = k_b T \quad (10)$$

where  $k_b$  is the Boltzmann constant. From normalization of  $P(E)$  and the average value of  $\langle E \rangle$ , we derive

$$P(E) = \beta \exp -E\beta. \quad (11)$$

### *The coarse-averaged Brownian motion equation for oscillators*

The first order Brownian motion equation gives for a collection of oscillator atoms a total system property [20, p.574] referring to the velocity  $v$

$$\langle (\Delta v(\tau))^2 \rangle = 2k_b T \gamma \tau / m \quad (12)$$

or

$$\langle (\Delta v(\tau))^2 \rangle = -2k_b T \langle \Delta v(\tau) \rangle / (m\bar{v}) >. \quad (13)$$

Writing the oscillator equation as  $X(t) = \langle X_0 \rangle \cos \omega t$  and averaging over the entire spectrum where  $\Delta v(\tau) = \ddot{X}(t) \tau$  we derive

$$\langle X_0^2 \rangle \tau \langle \omega^4 \rangle / 2 = 2 \langle \gamma \rangle k_b T / m \quad (14)$$

The average value of  $\omega^4$ ,  $\langle \omega^4 \rangle$  is

$$\langle \omega^4 \rangle = \int_0^\infty \omega^4 P(E) dE = 2/(\beta \xi)^2 \quad (15)$$

where  $\xi = m \langle X_0^2 \rangle$ . In the first order derivations here, we assume the following  $\langle \langle X_0^2 \rangle \rangle \approx \langle X_0 \rangle^2 \approx \langle \langle X_0 \rangle^2 \rangle$ , and when these do not hold one can always revert to the exact expressions. From (12,14,15) we derive

$$\tau k_b T = \langle X_0^2 \rangle \gamma m / 2 \quad (16)$$

$$= \langle X_0^2 \rangle a / 2. \quad (17)$$

The  $\gamma$  term is the average term  $\langle \gamma \rangle$ . We term equation (16) the First Certainty Relation, where we note that  $k_b T \sim \Delta E$ ,  $\tau \sim \Delta t$ , so that a classical statistical analog



to the Heisenberg Uncertainty Principle is represented by First Certainty Relation. The  $\gamma$  viscosity term pertains to all the oscillators, but the elastic constant  $k$  is obviously a variable ( $= \omega^2/m$ ) and its average  $k$  is

$$\langle k \rangle = 2k_b T \langle X_0^2 \rangle. \quad (18)$$

Combining (18) and (16) we derive the Second Certainty Relationship defined as

$$\gamma m / (\tau \langle k \rangle) = 1. \quad (19)$$

### *Radiation power and scattering*

Eqn.(6) involved a material matrix so that the damping term  $\gamma = a/m$  is ordinarily a mechanical quantity[20, p.565, Sec.15.6]; in our case it involves the strong electromagnetic forces and the much weaker dispersion forces of the particles, which in many instances may be neglected, as in the Poisson-Boltzmann solution of charges in a temperature field. This work maintains an open view concerning these interactions in that both the strong electromagnetic forces and the much weaker dispersion forces are included. If a direct equation is made to only electromagnetic damping, then  $Q\omega^2 = \gamma m/2$  where  $Q = e^2/(12\pi\epsilon_0 c^3)$ ,  $e$  being the charge,  $\epsilon_0$  the permittivity and  $c$  the phase velocity of the radiation. It is anticipated that in many cases this identity is a sufficiently accurate one. From (9), we can approximate that the average energy is maintained at  $\bar{E} = mX_0^2\omega^2/2$  over approximately one cycle before the mode reconstitutes itself into another mode. We note that the electromagnetic dissipation per unit time for strong electromagnetic interactions would be  $\gamma\bar{E}$ . A coarse-graining of the EM scattering over time  $\tau$  yields

$$-(d\bar{E}/dt)\tau = a \langle X_0^2 \rangle \omega^2 \tau / 2 \quad (20)$$

For  $N$  scattering centers, the total average radiation scattered  $\delta R(\omega)$  over time  $\tau$  is

$$\delta R(\omega) = a \langle X_0^2 \rangle N 4\pi^2 v^2 \tau P(E) d\bar{E} / 2 \quad (21)$$

for frequency range  $\omega - \delta\omega/2 \leq \omega \leq \omega + \delta\omega/2$  where the frequency  $v$  is related via  $\omega = 2\pi v$ . Clearly,

$$d\bar{E} \equiv 2\alpha\omega d\omega \quad (22)$$

$$\equiv 8\alpha\pi^2 v dv \quad (23)$$

where  $\alpha = m \langle X_0^2 \rangle / 2$ , and  $a = \gamma m$ .

For a conducting BB cavity, the number density  $D(v)$  per unit volume is given [21, p.118] by

$$D(v) = 8\pi v^2 c^{-3}. \quad (24)$$

Define  $\Omega = a \langle X_0^2 \rangle N 4\pi^2 / 2$ . Then

$$\begin{aligned} \delta R(\omega) &= P(E) \Omega v^2 \tau d\bar{E} \\ &= 8\Omega v^3 \alpha \pi^2 p(v) \tau dv \end{aligned} \quad (25)$$

where  $p(\nu) = P(E)$ . It is clear that the  $\delta R(\omega)$  function determines the frequency range in which radiation may be scattered, and which may be accepted by the blackbody cavity since it is in a resonance condition. Over time  $\tau$ , the energy received per mode is  $\delta r(\omega)$  where

$$\delta r(\omega) = \delta R(\omega)/(D(\nu)d\nu) \quad (26)$$

$$= c^3 \alpha \pi \Omega \nu p(\nu) \tau. \quad (27)$$

Define  $\varepsilon(\nu) \equiv \delta r(\omega)$ , which is the quantum of energy transfer over relaxation time  $\tau$ . From the First Certainty Relation (16), we write

$$\varepsilon(\nu) = 4c^3 \alpha \pi^3 N \tau^2 k_b T \nu p(\nu). \quad (28)$$

We notice that a frequency factor  $\nu$  appears for the quanta injected into the stable modes present in the cavity. The problem now is the possible temperature dependency. We note that we have carried our various coarse grained averaging, but the probability term (11) has a  $\beta$  pre-exponential term which cancels with the  $k_b T$  term of (28). There remains the  $\exp(-\beta E)$  term. Two arguments will be adduced to produce an expression for the quantum, one being an approximation :

(i) From equipartition, the average energy for each of the equilibrium vibration modes irrespective of frequency injecting radiation into the stable cavity modes is given by (11) so that we have  $\exp(-\beta E) = \exp(-k_b T/(k_b T)) = e^{-1} = \chi$ .

(ii) If a non-equilibrium oscillator energy density is involved, then subjected to the approximations of our averaging procedure, the term in the exponential  $-\beta E$  reduces from the First Certainty Relationship to  $\frac{-4\pi^2 \nu^2 \tau}{\langle \gamma \rangle}$ . The identity  $\omega^2 = k/m$  and the Second Certainty Relationship leads to the expression  $\exp(-\beta E) = \exp(-\frac{k}{\langle k \rangle}) = \chi(k)$ . Since the vibration constant varies slightly, being larger for higher angular frequency  $\omega$ , there would be a slight change of  $\chi$  depending on the frequency, but where nevertheless  $\chi(k) \approx e^{-1}$ . Much more experimentation and higher order stochastic analysis is required to determine which of the two scenarios is more likely. In this work, we write  $\chi$  as referring either to  $\chi(k)$  or  $\chi = e^{-1}$ .

From the above, the quantum  $\varepsilon$  of energy transfer over time  $\tau$  (28) can be written

$$\begin{aligned} \varepsilon(\nu) &= h\nu \\ &= 4c^3 \alpha \pi^3 N \tau^2 \chi \nu \end{aligned} \quad (29)$$

The BB Planck constant  $h$  may therefore be written in the case of complete scattering as

$$h = 4c^3 \alpha \pi^3 N \tau^2 \chi. \quad (30)$$

It is conceivable that the oscillators may not be in the proper position for affecting the radiation modes. Then an orientation factor  $\kappa$  must be factored into the Planck constant so that the effective Planck constant  $h_{eff}$  with orientation factor  $\kappa$  is written  $h_{eff} = \kappa h$  with  $h$  given in (30). The average power  $\langle P \rangle$  emitted by our oscillators is given by

$$\langle P \rangle = \langle \gamma m X^2 \rangle = a \omega^2 \langle X_0^2 \rangle / 2 \quad (31)$$



Equating (31) with the First Certainty Relationship yields  $\langle P \rangle = \omega^2 \tau k_b T$  and averaging (31) a second time yields

$$\langle\langle P \rangle\rangle = \gamma k_b T. \quad (32)$$

Eq.(32) was a very surprising result for it shows that the surface oscillators emit radiation in a manner that resembles Fourier heat conduction, and not as  $T^4$  as inferred by many from the Stefan-Boltzmann law for 3-D cavity radiation. Thus this coarse averaging theory predicts that a 2-D metallic or conducting sheet has essentially a Fourier heat transfer mechanism for thermal radiation, whereas if the topology of the system allows for cavity radiation buildup, then some  $T^4$  radiation transfer would also be possible. These result were verified in experiments conducted at the University of Malaya Engineering Faculty in the 1990's [22, 23].

### *The Planck distribution without recourse to the Second law*

For any one cavity mode, the average energy  $\bar{E}$  due to the scattered quanta is

$$\bar{E} = \lim_{M \rightarrow \infty} \sum_{n=0}^M n P(\varepsilon(\nu)n) \varepsilon(\nu). \quad (33)$$

Since the canonical distribution gives

$$P(n\varepsilon(\nu)) = \exp[-n\varepsilon(\nu)/(k_b T)] / \sum_{m=0}^{\infty} \exp[-m\varepsilon(\nu)/(k_b T)] \quad (34)$$

the two preceding equations (33,34) yield

$$\begin{aligned} \bar{E} &= \varepsilon(\nu) \exp[-\varepsilon(\nu)/(k_b T)] / (1 - \exp(-\varepsilon(\nu)/(k_b T))) \\ &= \varepsilon(\nu) / (\exp(\varepsilon(\nu)/(k_b T)) - 1). \end{aligned} \quad (35)$$

The total energy density for this particular mode  $U_\nu$  per unit frequency and unit volume is

$$\begin{aligned} U_\nu &= D(\nu) \bar{E}(\nu) \\ &= 8\pi c^{-3} \nu^2 h\nu / (\exp(h\nu/(k_b T)) - 1) \end{aligned} \quad (36)$$

which is the Planck formula [24, 25].

## **EXPERIMENTS AND THEORETICAL CONSEQUENCES**

*Experimental results: active heating experiments.* A thermal conductivity apparatus meant to demonstrate the standard radiation and convective heat transport laws at low pressure was modified [25] for our purposes. It consists of a cylindrical chamber that can be evacuated to low pressures by a single-stage pump of diameter  $2r_0 = 26$  cm and

length  $L_0$  of approximately 20 cm where in the center, a pencil-like heater (effective length 11.5 cm, diameter 1.03 cm with heating area of  $38.4 \text{ cm}^2$ ) was clamped in place by insulated holders. This arrangement leads to an unambiguous determination of the convective heat transfer coefficient at the indicated vacuum pressure which may be compared with available data and we found that our foil samples were in accord with the standard data [23, Sec. 3]. The temperatures were monitored by very thin (fine) thermocouples. By various methods of calibration and extrapolation (for instance from a  $\Delta T \text{ vs } (P)^{1/4}$  power law ( $P$  being the pressure) at fixed electrical power dissipation to determine the actual temperature difference at zero pressure between the heater and chamber wall) we can determine the actual transfer of radiation in the pure vacuum state. Also, we can eliminate through extrapolation the heat conduction due to the thermocouple wires, the holders and the residual convective transfer due to the low pressure gas present. (The lowest gas pressures attainable was  $\approx .166$  mbar. Because various surfaces are present, each of which transmits radiation with the  $I_0 \cos \theta$  Lambert law applying, one can through integration for various geometries calculate the net transfer of energy from surface  $S_1$  to  $S_0$  where  $S_0$  is the outer chamber and  $S_1$  is the thin pencil heater surfaces respectively. For the ratios  $L_0/r_0 = 19/13$ , and  $r_1/r_0 = .038$  [24, Fig.8-159(b),p.322] the energy transfer ratio from  $S_1$  to  $S_0$  is  $\approx 98\%$  which warrants the energy transfer expression (normalised to  $1 \text{ m}^2$  of surface  $S_1$ ) due purely to heat radiation because of a temperature difference  $P_w$  to

$$P_w = \gamma_d(T - T_0) + \sigma(T^4 - T_0^4) \quad (37)$$

where  $T_0, T$  are respectively the temperatures of the chamber and metallic sample wound round the pencil heating element. If  $T = T_0$ , then there is no net radiation heat transfer  $P_w$  which explains the form of (37). We carried out experiments for both the active heating of sheets and also for the passive relaxation (cooling) of solid metallic cylinders (as opposed to sheets). For active heating of sheets, we used 4 different metal specifications, the one reported here is material C1 [Cu, 99.9%, Phosphorus deoxidized, BS2870/JSH3100, 0.127mm rolled sheet]. For another temperature differential experiment we also use material A1, A1 [Al,(ALCOM,MALAYSIA) 99.6%,AA1100-H24 Finstock,0.115mm rolled sheet]. Because we can measure and extrapolate all parameters, the active heating experiments are more accurate. Define the mean power square deviation  $ASD[L]$  as

$$ASD[L] = \sum_{i=1}^N P_{wi} - \gamma_d(T_i - T_0) - \sigma(T_i^4 - T_0^4))^2 / N. \quad (38)$$

Let the label  $[L]$  denote the following situations in the optimization: 1)  $\gamma_s$  when the *single* optimization involving only  $\gamma_d$  is involved where  $\sigma = 0$ , 2)  $\sigma_s$  when the *single* optimization involving only  $\sigma$  is involved where  $\gamma_d = 0$ , 3)  $\gamma_c \sigma_c$  when *both* parameters are optimized by standard least squares optimization; in all cases the  $\gamma_d$  and/or  $\sigma$  values are given by the  $s$  or  $c$  subscript. The results for the C1 material with  $T_0 = 302.9\text{K}$  is presented as a set with the key  $\{T_{ave}, \gamma_s, \sigma_s, \gamma_c, \sigma_c, ASD\gamma_s, ASD\sigma_s, ASD\gamma_c\sigma_c\}$  where  $T_{ave}$  is the average temperature of the measurements for the  $(\sigma, \gamma)$  parameters, where 100 equally spaced intervals in  $P_w$  were used for each set. We have for material C1  $\{420.2, 4.470, 0.2287 \times 10^{-7}, 3.737, 0.3754 \times 10^{-8}, 13.375, 325.3, 0.8899\}$  and



$\{449.6, 4.597, 0.2061 \times 10^{-7}, 2.910, 0.7566 \times 10^{-8}, 74.97, 217.4, 2.884\}$ . The  $R_d$  ratio of radiant dissipation defined as  $\gamma_c(T - T_0)/\sigma_c(T^4 - T_0^4)$  is approximately 4 : 1 in most cases or greater for all our active heating experiments ( $> 5 : 1$  in the second set). In nearly all our measurements [22, Tables 2-5]  $ASD\gamma_s < ASD\sigma_s$ , implying the superiority of the linear to the  $T^4$  power law, but the combination law is often the best because there are more variables present. These results seem to underscore the importance of the linear law.

*Minor measured equilibrium temperature differences.* These experiments are semi-quantitative, but the measurements are significant to within experimental error. The spot-welded tips of the two thermocouples were put in contact and observed in vacuo ( $\approx 0.16$  mbars) where no change to  $\sim 0.1$ K could be detected. Materials A1 and C1 were rolled from a flat sheet  $13 \times 19.4$  cm to a cylindrical object (with 0.4 cm overlap) and were fastened with transparent tape (Sellotape) and suspended centrally with very fine cotton thread with 2cm clearance from the base of the cavity in its natural state and the top was covered with a flat plate painted matt black as was the color of the well. At atmospheric pressure, the maximum temperature difference between the rolled A1 sheet (at T1) and the vessel wall (at T2) was .1K, the vessel being warmer in several repeated experiments. As the pressure dropped, we get the results  $\{P(\text{mmHg}), T1(^{\circ}\text{C}), T2(^{\circ}\text{C})\}$  such as  $\{0.125, 25.6, 26.1\}$  and  $\{0.120, 25.7, 26.2\}$  after equilibrating (no change of temperature in a 10-minute interval). For C1, typical results are  $\{0.15, 24.6, 25.0\}$ ,  $\{0.125, 25.1, 25.5\}$ ,  $\{0.10, 25.4, 25.7\}$ . A statistically significant difference of 0.5-0.3 K is noticed. The same magnitude of temperature differentials is observed if the wall lining is replaced by the same material as the test sample. These may be due to other effects connected with e.g. heats of desorption or chemical changes on the surfaces but the temperature difference persisted as long as observation was made ( $\sim 1$ -3 hours) and so could also be attributed to an actual temperature difference between the surfaces considered free from physical and chemical effects. The best method to check for variation would involve measurement without metallic contact (since thermal material conduction as exists in the thermocouple wires would tend to negate the effects of thermal variation) e.g. laser light reflection analysis, where if there are discernible effects, they would probably be of a higher magnitude than the crude results obtained here because of thermal conduction due to the wires. Nevertheless, these experiments consistently show a significant temperature variation of approximately 0.5K in all of the experiments under equilibrium conditions.

*Some theoretical consequences.* We outline just 5 of several possible consequences of the above experiments if they turn out to be valid that comes from (i) the partitioning of the surface processes and the bb cavity radiation (ii) the linear form of radiation transfer from a surface (iii) considerations of the bb cavity and temperature differentials that leads to the generalization of the Kirchoff radiation law (iv) statements and theorems for equilibrium temperature differentials and (v) entropy conjectures for these systems.

(i) *Pure bb emissions from a cavity with variable index of refraction.* The index of refraction  $n$  is frequency ( $\nu$ ) dependent if dispersion [26, Chap. 19] is considered, so that  $n = n(\nu)$ . We may consider statistical scattering of energy by the surface oscillators over every element  $d\nu$  of frequency  $\nu$  in a standardized bb cavity of unit volume having  $N$  oscillators, a mean relaxation time  $\tau$ , where  $\alpha = m < X_0^2 > / 2$  and where all these variables are as defined above for the bb development. Since the elementary quantum



$\varepsilon = \delta r(\omega)$  is, from (26), dependent on  $D(\nu)$ , then if the index of refraction of the 3-dimensional bb cavity is  $n = n(\nu)$ , we expect a modification to the radiancy from such a bb.  $D(\nu) = 8\pi\nu^2 c_m^{-3}$ , where  $c_m$  is the velocity of light in the medium of refractive index  $n(\nu) = c/c_m$ , and  $\lambda_m \nu = c_m$  where  $\lambda_m$  is the associated wavelength;  $\nu$  does not change when light travels through two media with different  $n$ 's, and we assume that such is the case of *em* waves transmitted between the surface oscillators and the bb cavity. From the definitions,  $D(\nu) = 8\pi\nu^2 c^{-3} n^3$  and from (25) and (26),  $\varepsilon$  must transform

$$\text{as } \varepsilon = \delta r(\omega) = \varepsilon' = h\nu n^{-3}. \text{ Since } \bar{E}(\nu) = \bar{\varepsilon}(\nu) = \frac{\sum_{n=0}^M n\varepsilon(\nu)p(\varepsilon(\nu)n)}{\lim_{M \rightarrow \infty}} \text{ where}$$

$$p(n\varepsilon(\nu)) = \exp -n\varepsilon(\nu)/k_b T \bigg/ \sum_{m=1}^{\infty} \exp -m\varepsilon(\nu)/k_b T$$

we derive  $\bar{E}(\nu) = \frac{\varepsilon(\nu)}{(\exp(\varepsilon(\nu)/k_b T) - 1)}$ . The Planck energy density is  $U_\nu = D(\nu)\bar{E}(\nu)$ , which therefore modifies to  $U'_\nu = 8\pi\nu^3 h c^{-3} / [\exp(\varepsilon(\nu)/k_b T) - 1]$ . The radiancy is

$$E'_{b\nu} = \frac{c_m U'_\nu}{4} = \frac{c U'_\nu}{4n} = (2\pi h \nu^3 / [n c^2]) [\exp(h\nu / [n^3 k_b T]) - 1]^{-1} \quad (39)$$

One the other hand, the standard result is [27, p.9]

$$E_{b\nu} = (2\pi h \nu^3 n^2 / [c^2]) [\exp(h\nu / [k_b T]) - 1]^{-1}. \quad (40)$$

However, Wiebert has pointed out [28, p.53] that this result is hardly ever used. From the above, we see that the Planck density derives from the canonical distribution function applied to the wave modes within the 3-dimensional cavity, whereas the  $\gamma k_b T$  energy emission or absorption term derives from applying a canonical probability function for oscillators with one or two degrees of freedom. Hence the dimensionality of the system is crucial to the energy density of radiation emitted by the system. The role of dimensionality has been neglected in normal heat transfer applications, where the 3-dimensional Planckian form is routinely assumed to hold for 2-dimensional surfaces [27, 28].

(ii) *Explanation for the results of active heating of surfaces experiments and preponderance of linear form of radiation transfer from such a surface.* The first order results from the theory above indicate a leakage current (32) of magnitude  $\ll P \gg = \gamma k_b T$  per oscillator on the 2-dimensional surface which should be compared to the Feynman emission density expression  $I(\omega) = \omega^2 k_b T / (\pi c)^2$  [19] which does not integrate to a finite value for a surface. His conclusion then is that there is something wrong with the classical equipartition since infinities are involved, in contradiction to experiment. However, here we have shown that no infinities are involved. The second effect observed experimentally is a minor  $< 20\%$  3-dimensional build-up of electromagnetic energy in sheets which becomes more pronounced for larger 3-D metallic objects  $\approx 50\%$  or coiled sheets that allow for cavity radiation buildup within the interstices. One must also account, in the case of a solid of the relatively weaker carriage of bb (meaning here  $T^4$  dependent radiation). These effects can be written in the following form where  $P_g(g, T)$



is the total emission per unit area of surface where  $\mathbf{g}$  are the geometrical variables

$$P_g(\mathbf{g}, T) = \Pi(\mathbf{g}, T)\sigma_s T^4 + \sum_{i=1} l_i(\mathbf{g})T^i + A(\mathbf{g}, T)\sigma_s T^4 \quad (41)$$

and where  $\sigma_s$  is the Stefan constant for bb radiation emitted from a standard cavity. In (32), it was assumed that  $\gamma$  was slowly varying with respect to  $T$ ; if it were expanded out in a Taylor series using a more complex theory than presented here, multiplied by  $k_b T$ , then the coefficients would be  $l_i$ . Coefficient  $A$  is some average coefficient due to the buildup of possible cavity radiation due to sheets that are coiled, allowing for small cavities, or microcavities due to surface morphology orientated in a particular direction;  $\Pi$  is a new type of bb permeability factor which determines the leakage of the bb-type radiation of the lattice which builds up as a result of the apparent excess charge density of the surface which scatters into the 3-dimensional lattice [29, p.100, eq.43], as well as the internal scattering of the radiation generated by the oscillators within the cavity[30, p.15]; this 3-D bb heat then permeates through the 2-D outer surface of the system. The quantum concept of surface charge arises from the Fermi level surface [30] whereas classically, one can evoke the construct of Poisson's equivalent distribution for materials with dielectric properties, where for a point  $P'$  outside the dielectric, the potential there is the same as that due to a volume distribution of density  $\rho_p = -\nabla \cdot \mathbf{P}$  and a surface distribution of density  $\sigma_p = \mathbf{P} \cdot \mathbf{n}$ , the normal component of  $\mathbf{P}$ , the polarization [30, p.15]. This dielectric simulation may be applied to a metallic conductor where there exists a separation of charge due to the mobile valence electrons, causing an instantaneous dipole for each atomic center. Equation(41) is not compatible with directly equating the bb component with a linear or other power law in temperature. Also, in a conducting media, the buildup of *em* radiation and the intensity of that buildup is different from that of the vacuum state. Indeed, attenuation of the *em* waves implies hardly any buildup of stable modes with large intensities. In such media, the attenuation of the *em* waves created at the surface is well described [26, Eq.(17-47)-(17-55)]. For a complex refractive index  $\hat{\mathbf{n}} = n + ik$ , the freely propagating wave  $\mathbf{E} = \mathbf{E}' \exp[-i(\omega t - \mathbf{u} \cdot \mathbf{r} \cdot n/c)]$  becomes  $\mathbf{E} = \mathbf{E}' [\exp(-k\zeta/c)] \cdot \exp[-i(\omega t - \mathbf{u} \cdot \mathbf{r} \cdot n/c)]$  with the attenuation factor  $\zeta$  which is a linear function of propagation distance. However, subject to the boundary conditions used to derive the vacuum bb radiation, each mode is independent with its own quasi partition function of form (5)  $(D_i)^{-1}$ , so that a Planck-type distribution is expected to ensue with a  $T^4$  density, but the parameters such as the Stefan constant would differ from a vacuum cavity since it would be a function of the internal variables such as the conductivity, permittivity etc. The permeability factor  $\Pi$  accounts for the changes of the partition functions due to attenuation (of the standing wave patterns) and the penetration of the waves through the surface layer with its charge density. The geometrical factors  $\mathbf{g}$  include structure such as a coiled sheet that can create standing wave patterns at the interstices of succeeding sheets in the coil, or a solid such as a cylinder where the standing wave pattern is found within it.

(iii) *Considerations of the bb cavity and temperature differentials that leads to the generalization of the Kirchoff radiation law.* For what follows, we make the assumption that indeed equilibrium temperature differentials according to the Kelvin scale can exist. We then deduce the consequences of such a result. In our experiments, temperature differentials persisted despite having the same material for the centrally placed object



as the wall of the apparatus. It follows that the different intensity of radiation falling generally on both surfaces is a factor in accounting for such changes. People have been accustomed to viewing radiation as a "substance" like matter, and therefore ascribed the same energy transfer properties. However, Planck has shown that if light be considered as particulate in its intensity  $I$  per unit time and area, then the pressure exerted on a metallic surface is only half of that due to Newtonian particles having the same intensity  $I$  [15, p.53, Sec.57-60] all at the same velocity. If equilibrium is concerned with force balance (as is the *general* assumption here) then systems "connected together" by a radiation field would not have the same forces acting on them as if they were "connected together" through diathermal contact by a Newtonian matrix of particles. The Boltzmann constant  $k_b$  is inferred in statistical mechanics from systems in mechanical contact [31, Chap.2] in an ensemble, where the traditional supposition has been systems which statistically obey Newtonian dynamics with respect to momentum interchange, whereas for pure heat radiation, the momentum contact exchange between the surfaces (i.e. energy interactions) need not necessarily involve the same temperature parameter (with respect to Newtonian molecular momentum exchange) if the Planck inference is valid and if it can be derived via the principles of statistical mechanics. Blackbody boundary matrixes (bm) where the charged oscillators reside have a Kelvin temperature because they are connected together in an ensemble that obeys Newtonian dynamics. Consider the system of standardized (meaning that the energy density is as given by the Planck law with the associated constants) unit volume bb cavities that possesses exactly similar dipole oscillators in the bm, and where the temperature is  $T_c$  for both the bm and bb radiation. The bb radiation is defined to be at temperature  $T_c$  because it is in equilibrium with the bm, whose temperature may be determined by mechanical contact with a thermometer involving Newtonian corpuscular momentum transfer. We may suspend a body of known geometry and material composition in the cavity until it reaches radiothermal equilibrium (without Newtonian corpuscular momentum transfer in the Planck sense). We define the traditional statement of the Zeroth law to imply Newtonian corpuscular momentum transfer (with conservation) amongst the systems in contact and refer to this implication as **ZLNM**. We may replicate this system  $A$  times (where the bm's are contiguous and in thermal contact) for  $A$  systems of cavities with identical radiation. By **ZLNM**, the bm's all have the temperature  $T_c$ . Since the suspended bodies are not in mechanical contact, we need not ascribe a Kelvin temperature  $T_c$  to it, although since they are exchanging energy with the bms, there must exist another parameter common to both, which must be determined. We suppose that the mean energy of a bm  $\bar{E}_{bm}$  and that of the suspended body  $\bar{E}(N, V)$  obeys  $\bar{E}_{bm} \gg \bar{E}(N, V)$ . Let  $E_j(N, V)$  be a microstate of the suspended body ( $N$  being the number of particles say and  $V$  its volume). By the stationary entropy principle and Boltzmann's modified definition of entropy  $S$  where for any composite system we write  $S_A = \Upsilon \ln \Omega_A$ , where  $\Upsilon$  is an undetermined constant and  $\Omega_A$  is the number of arrangements consonant with energy and mass conservation. We note that in the normal optimization methods, one either stationarizes  $\ln \Omega$  or  $\Omega$  where the  $\Upsilon$  factor is not relevant. It becomes relevant only when the entropy is standardized. From these definitions it follows (for details of the standard methodology see [31, Chap. 2]) that for the suspended object the probability of state  $j$   $P_j$  is given as  $P_j = \exp[-\beta E_j(N, V)]/Q$ , where the partition function is  $Q = \sum_j \exp[-\beta E_j(N, V)]$  and the average value  $X$  of thermodynamic variable  $X_j$  in



state  $j$  is  $\bar{X} = \sum_j X_j P_j$ . We now consider two situations: a') the bm's of each individual system denoted  $A$  without the smaller body  $C$  suspended in any of them, where the bm's now compose a canonical ensemble and b') the ensemble as in a') but with  $C$  suspended in each of the systems enclosed by the bm's. Since  $E_{bm} \gg E(N, V)$ , each bm is a thermal reservoir [20, p.202, Sec. 6.2] with respect to the  $C$  suspended within. For a'), each bm subsystem would [31, eq.2-12] constitute a separate entity with **ZLMN** interaction and with temperature parameter  $\beta$ , where the probability of the bm energy state  $E'_j$  of a particular bm is  $P'_j = \exp -\beta E'_j(N, V)/Q$ . The connection between  $\beta$  of statistical mechanics and macroscopic thermodynamics (where the Kelvin temperature  $T$  is featured) is made by comparing (i)  $(\partial E/\partial V)_{N, \beta} + \beta(\partial P/\partial \beta)_{N, V} = -P$  with (ii)  $(\partial E/\partial V)_{N, T} + T(\partial P/\partial T)_{N, V} = -P$ , where  $P$  is the pressure, and the other symbols as previously defined. The ensemble postulate of Gibbs relates directly any macroscopic thermodynamical variable  $X$  with ensemble average, i.e.  $\bar{X} = X$  (with the exception of all global parameters as  $\beta$  and  $\mu$ , the chemical potential per particle). From (i) and (ii), it is inferred that  $\beta = 1/k_b T$  for bm systems in a'), where  $k_b$  is the Boltzmann constant. By considering another system  $B$  in thermal **ZLMN** contact with  $A$  to form a system  $AB$  which is one member of like systems  $AB$  in an ensemble, it can be shown (assuming independence of  $\Omega_A$  and  $\Omega_B$ ) that  $A$  and  $B$  [31, Chap.2] must have the same  $\beta$ ; by inference from the Zeroth law in the **ZLMN** sense, where  $A$  and  $B$  are in interaction via Newtonian corpuscular interaction at the same pressure  $P$ , then the Kelvin temperature  $T$  must be the same, where  $k_A T = k_B T$  or  $k_A = k_B = k_b$ , where  $k_b$  is universal for **ZLMN** thermal equilibrium. Thus, the  $k_b = k$  value for the bm's (system  $A$ ) is fixed and equal to the Boltzmann constant  $k_b$ . For case b'),  $A$  the bm and  $C$  the suspended object are in radiothermal contact, in non-**ZLMN** interaction. By repeating the derivation as for **ZLMN** contact, where in statistical mechanics the only assumptions for the canonical ensemble are 1) energy and mass conservation, 2) independence of probability distributions of the microstates in systems  $A$  and  $C$  [31, Chap.2], we again derive that for systems  $A$  and  $C$ , the same  $\beta$  obtains. But from a'),  $\beta = 1/k_b T_A$ , hence

$$k_b T_A = k_C T_C \quad (42)$$

where the  $T$ 's are the Kelvin temperatures that can be determined by a "diathermal fibre" [32] and where  $T_A$  need not equal  $T_C$ . The contact term  $k_C$  is relative to any of the systems in radiothermal contact with it, such as system  $A$  and is called the radiothermal constant for body  $C$ . Suppose in nested Chinese box fashion we suspended object 1 inside object 0 (which has  $k_0 = k_b$ ), and 2 inside 1, 3 inside 2 and so on. Then

$$k_0 T_0 = k_1 T_1 = \dots = k_n T_n \quad (43)$$

and in the limit, the surfaces would be infinitesimally separated. Hence for a system whose components are radiothermally in equilibrium, where in traversing a path  $L$  of independent thermodynamical coordinates, we derive the elementary expression for the radiothermal constant  $k$  and the temperature for system  $\alpha$  (used to denote to which system the variables refer to) between any two points  $L_1, L_2$  in thermodynamical space a type of reciprocal relation

$$\int_{L_1}^{L_2} T_\alpha dk_\alpha = - \int_{L_1}^{L_2} dT_\alpha k_\alpha \quad (44)$$



and since  $\Phi_\alpha = k_\alpha T_\alpha = \text{const}$ ,  $d\Phi = 0$ , implying trivially that  $\oint d\Phi = 0$  or that  $\Phi_\alpha$  is a perfect differential. Suppose there are  $n$  nested Chinese boxes inside system 0, then assuming that the temperature distribution is due to the first  $q$  boxes and at the same time for all  $n$  where (43) obtains, we obtain for the  $q^{\text{th}}$  box results such as

$$\begin{aligned} T_q &= \frac{(k_0)^n}{\prod_{i=1}^n k_i \prod_{i \neq q}^n T_i} \\ &= \frac{(k_0)^q}{\prod_{i=1}^{q-1} k_i \prod_{i \neq q}^{q-1} T_i} \end{aligned} \quad (45)$$

The above deduction come from what is termed the series arrangement. The parallel arrangement is when "small" bodies  $C_1, C_2, \dots, C_n$  are simultaneously suspended in cavity  $A$ , where  $\sum_i E_{C_i} \ll E_A$ , so that the radiation in the cavity  $A$  is determined by  $A$  only. Then if the systems  $C_1 \cup A, C_2 \cup A, \dots, C_n \cup A$  are all considered independent, the previous arguments would yield

$$k_b T_A = k_{C_1} T_{C_1} = k_{C_i} T_{C_i} \quad (i = 1, 2, \dots, n) \quad (46)$$

Write  $k_{C_i} T_{C_i} = k_{C_i} T_{C_i}(\mathbf{G}, \mathbf{A})$  where  $\mathbf{G}$  are variables for the particular body suspended in  $A$  (including geometrical variables) and  $\mathbf{A}$  are the thermodynamical variables for  $A$ . There are several possibilities concerning the dependence of the  $k$ 's on  $(\mathbf{A}, \mathbf{G})$ . If there is dependency only on  $\mathbf{A}$  then there will be equal temperatures for all  $C_i$  and all the  $k$ 's will be the same even if not the same as  $T_A$ ; if there is dependency on both these variables then the temperatures could be different. There are many of these possibilities to consider that experiment alone will help determine.

*The Kirchhoff radiation law generalization.* The generalization is readily made from the results above with the principle of detailed balance on each surface of a body  $C$  immersed in a radiation field; traditionally, it has been presupposed that the radiation field is a standard bb field with incident radiation  $P_i(\mathbf{k}, \alpha, \beta^{-1})$  where  $\beta^{-1} = k_b T$ . The body's emissivity  $P_e^C$  [20, Sec. 9.15] is defined such that

$P_e^C(\mathbf{k}, \alpha) d\omega d\Omega$  = the power, per unit area emitted with polarization  $\alpha$  into a range about wavevector  $\mathbf{k}$  between angular velocity  $\omega$  and  $\omega + d\omega$  about direction  $\mathbf{k}$ .

Then the principle of detail balance is applied where

Power radiated by body = power absorbed by the same body.

Apply these principles to our body  $C$  suspended in the cavity of a standardized bb where  $\beta^{-1} = k_C T_C$ , we deduce that

$$P_e^C(-\mathbf{k}, \alpha, \beta^{-1}) / a^C(\mathbf{k}, \alpha, \beta^{-1}) = P_i(\mathbf{k}, \alpha, \beta^{-1}) = f_A(\beta^{-1}) \quad (47)$$

or

$$P_e^C(-\mathbf{k}, \alpha, T_C k_C) / f_A(\beta^{-1}) = \epsilon_C = a^C(\mathbf{k}, \alpha, \beta^{-1}) \quad (48)$$

where  $P_e^C$  is the emission in direction  $\mathbf{k}$ ,  $a^C$  the absorbance of the object  $C$  at the same Kelvin temperature as the object  $T_C$ ,  $P_i$  the incident radiation of the standardized radiator  $A$  which is a function of  $\beta^{-1} = T_C k_C = k_b T$  only, so that  $P_i = f_A(\beta^{-1})$ . The emissivity  $\epsilon_C$  is defined with respect to  $A$  and no similar temperature is required i.e.  $T_C \neq T = T_A$



in general.

(iv) *Statements and theorems for equilibrium temperature differentials.*

We now define the temperature factor  $\beta^T$  to have the form of inverse  $\beta$  i.e.  $\beta^T = k_i T$  for some coupling coefficient for system  $i$  where in general  $k_i \neq k_b$ . If thermal energy is injected into a system initially at radiothermal equilibrium (between object  $j$  and  $A$ ) with temperature  $\beta_{eq}^T$ , say at surface  $j$ , then it would heat up leading to a temperature rise until  $\beta_j^T > \beta_{eq}^T$  and if left to relax with the other surface at  $A$  maintained at a fixed temperature throughout, there would be flow of energy from  $j$  to  $A$  until another equilibrium temperature  $\beta_{eq}'^T$  is reached. We generalize heat energy as that form of energy that flows as a result of a temperature difference  $\Delta\beta^T$ . Thus a flow of this heat from a 'hotter' to a 'colder' region is anticipated with increase in entropy, even if the term 'hotter' or 'colder' is contradicted where the Kelvin temperature  $T$  is considered because it is possible for  $\beta_i^T > \beta_j^T$  even if the Kelvin temperature  $T$  with subscripts denoting the system is such that  $T_i < T_j$ . Since heat is well defined here, we also define a dimensionless radiothermal entropy  $S^{rd}$  increment as  $dS^{rd} = dQ/\beta^T$  for heat increment  $dQ$  for heat variable  $Q$ . Further, we also define the flow of energy by virtue of a temperature difference  $\Delta\beta^T$  as conductive heat flow. Then the entropy change for each type of radiothermal heat flow is always positive, as is the case with pure conductive heat flow without coupling, since if  $\beta_j^T > \beta_{eq}^T$  for the  $\{j, A\}$  system, then for the flow of heat  $Q$  transported from  $j$  to  $A$  when subjected to the temperature differential,  $\Delta S^{rd} = -Q(1/\beta_j^T - 1/\beta_{eq}^T) \geq 0$  which is a Second law deduction. Relative to radiothermal coupling, even if  $T_j < T_{eq}$ , there can still be conductive radiothermal transfer from  $j$  to a point at  $A$  at temperature  $T_{eq}$  provided  $(k_{eq}/k_j) < 1, T_j \geq (k_{eq}/k_j)T_{eq}$ . We denote the heat current vector due to heat flowing by a non-ZLMN form of interaction  $i$  as  $\mathbf{J}_{qi}$ .

The above implies that the Fourier Principle as explicated by Benofy and Quay [32] regarding radiation transfer cannot be correct (it may be termed correct for ZLMN type heat transfer only) and demands generalization. For conductive (ZLMN) heat transfer, the principle states that  $\mathbf{J}_q \cdot \nabla T \leq 0$  always, where  $T$  is the Kelvin temperature and  $\mathbf{J}_q$  the conductive heat transfer. We generalize this by stating that for pure conductive heat transfer via energy form  $i$  (non-ZLMN) in thermal equilibrium with distinctly different energy form  $j$  (also non-ZLMN) and form due to ZLMN processes with conductive (as opposed to other types of energy transfer [32]) heat vector  $\mathbf{J}_q$ , we have each of the following holding simultaneously and separately;  $\{\mathbf{J}_{qi} \cdot \nabla \beta_i^T \leq 0, \mathbf{J}_{qj} \cdot \nabla \beta_j^T \leq 0 \text{ and } \mathbf{J}_q \cdot \nabla T \leq 0\}$ , where  $\beta_i^T(\mathbf{R}) = k_i T_i$  for all  $i$  non-ZLMN processes, and  $k_i$  is a function of geometry and thermodynamical variables  $\mathbf{R}$  and is the coupling constant discussed previously. For discrete surfaces, the gradient  $\nabla \beta_i^T$  is replaced by  $\nabla \beta_i^T \approx \delta \beta_i^T / \delta l = (\beta_{S2i}^T - \beta_{S1i}^T) / \delta l$  to compute the gradient for heat transfer between surfaces  $S1$  and  $S2$ . Clearly, the conventional definition of heat in thermodynamics is then equivalent to conductive heat as defined here (for further details see reference [32]) for ZLMN type interactions. By definition of our generalized conductive heat, assuming continuous behavior of the variables and heat transfer rates, the rate of heat transfer would be a function of the temperature difference per unit length, so that first order Fourier-like equations for conductive heat for each of the different energy forms  $i$  and  $j$  is envisaged,



and may be written for each  $i$  as follows

$$\mathbf{J}_{qi} = -K_i \cdot \nabla \beta_i^T \quad (49)$$

where  $K_i$  is the conductivity tensor and  $\nabla \beta_i^T$  the generalized temperature gradient, where  $\nabla \beta_i^T = k_i T_i$ .

This work has stressed on the coupling due to electromagnetic waves but the above terminology "energy form" may refer to all other non-ZLNM processes, including possibly gravitational heat or thermal waves as well for interactions  $i$  or  $j$ . Eq. (49) may be generalized to any order, as is true for normal Fourier conduction as well. We have demonstrated experimentally that (49) could be the main form for radiation transfer from a flat 2-D structure and its surface. This possibility opens to question work that uses previously developed potentials [33] to model a  $bb T^4$  power law [34, see esp. Annex A and Sec. 2, p.216]

*General equilibrium criterion and consequences.* Focus on any one particle or quasi-particle or "complexed quantum" [35, 36] and monitor its change of momentum for  $n$  collisions as  $n \rightarrow \infty$  and where we fix the time increment  $\delta t_i = \delta t$  for all collisions  $i$  and where  $F_i$  denotes the force on the particle for the  $i$ th interaction. Then

$$\sum_{i=1}^n F_i / n = \bar{F} \rightarrow 0$$

for equilibrium or else the momentum and absolute magnitude of the energy of the system will keep increasing in contradiction to the definition of the equilibrium state. Since  $\sum_i^n F_i \delta t = \sum_i^n \Delta p_i$ , then  $\sum_i^n \Delta p_i / n \equiv \overline{\delta p} \rightarrow 0$  and a necessary condition for equilibrium is that the mean momentum change for any particle must be zero. Consider then two  $bb$  cavities 1 and 2 in radiothermal equilibrium with Planck factors  $h_{m_1}(T_1)$  and  $h_{m_2}(T_2)$  respectively. The apparent momentum of each photon of frequency  $\nu$  is  $h\nu/c$  so that the above equilibrium principle leads on averaging of transitions from 2 to 1 as

$$\begin{aligned} & (< h_{m_1}(T_1) > \nu - < h_{m_2}(T_2) > \nu) / c = 0 \\ & \text{or} \\ & < h_{m_1}(T_1) > = < h_{m_2}(T_2) > . \end{aligned} \quad (50)$$

Hence the Planck factor must be the same for all cavities that are simultaneously in equilibrium. What about nonlinear quanta, a possibility suggested by (30) for non-constant  $\chi$ ? At this point we are in the realm of pure conjecture. If there is some possibility for nonlinear quanta, then higher frequency waves would lead to a relatively smaller value of  $h$  and vice versa since  $\chi = \exp -(k / < k >)$ . Thus this situation could lead to a cross-coupling of different quanta as they traverse from one cavity to another in radiothermal equilibrium since the net momentum change must be zero. Thus if cross-coupling (or transmutation) is admitted, then with the same notation as above, we have

$$\begin{aligned} & (h_{m_1}(\nu_1, T_1) \nu_1 - h_{m_2}(\nu_2, T_2) \nu_2) = 0 \\ & \text{or} \\ & \frac{h_{m_1}(\nu_1, T_1)}{h_{m_2}(\nu_2, T_2)} = \frac{\nu_2}{\nu_1} \end{aligned} \quad (51)$$



Theoretically the above should also obtain for intra-cavity radiation if nonlinear quanta exists. The Planck factors relative to the different temperatures and frequencies could also represent stochastic averages.

(v) *Entropy changes in radiathermally coupled systems.* If two bodies are in radiathermal equilibrium, then if the two are coupled by a Carnot engine via **ZLNM** surface interactions, then work can be extracted from the system based on **ZLNM** interactions if their Kelvin temperatures differed; further if they are connected directly by **ZLNM** interactions without the intervention of a Carnot engine, so that there is conductive heat flow, then there would be an increase of standard **ZLNM** entropy  $dS = -dQ(1/T_1 - 1/T_2) > 0$  at the indicated temperatures  $T_1 > T_2$  with a transfer from body 1 to 2. On the other hand, radiathermally, they would be at the same temperature  $\beta^T$  and the radiathermal entropy change would be zero  $dS^{rd} = 0$ . Thus the two forms of entropy are not directly equatable at this level of development. Similarly, if a system is at radiathermal equilibrium with the indicated Kelvin temperatures, then a Carnot engine working perfectly according to **ZLNM** interactions would cause an entropy change  $dS$  of zero, whilst doing positive work  $W$  on the environment of amount  $dQ_1 - dQ_2$ , where the heat absorbed by the engine at body surface 1 is  $dQ_1$  and that ejected at body surface 2 is  $dQ_2$ , where  $dQ_1 > dQ_2 > 0$ . On the other hand, the radiathermal entropy change would be such that  $\frac{dQ_1}{k_1 T_1} > \frac{dQ_2}{k_2 T_2}$  or from the previous inequality  $dS^{rd} < 0$ . It was conjectured, on the other hand that if the Carnot engine were radiathermally coupled to the temperature sources of the system, then for heat transfer increments  $dQ$  due to radiathermal (non-**ZLNM**) interactions, [23, p.27,eq.14] where the radiathermal temperature is  $\beta^T = k(\mathbf{R})T =$  we get

$$\oint dS^{rd} = \oint dQ/\beta^T = \oint dQ/(k(\mathbf{R})T) = 0 \quad (52)$$

so that  $dS^{rd}$  is a perfect differential about thermodynamical space  $\mathbf{R}$  with  $k$  the coupling coefficient.

## CONCLUSIONS

It is possible to reconcile from classical Brownian motion considerations the experimental outcome of a linear term in temperature of the radiant heat flux, and that the physical dimensionality of the system must be considered in determining whether bb radiative flux is the principle form of heat transfer or not.

Considerations concerning the density of state and the nature of the Planck quantum in terms of the relaxation time of all the surface oscillators of a bb cavity lead to another form of the radiancy expression in the presence of a medium with refractive index other than unity.

From the postulate that different energy coupling schemes based on the different laws of nature are possible, there exists the possibility of minute temperature differences at "radiathermal equilibrium", and in the event of this possibility, our theories result in the extensions of the Zeroth, Kirchoff, Second and Fourier Heat Conduction laws. Our elementary experiments suggests such possibilities. This analysis can be extended to



other forms of energy interactions resulting in the same structure of coupling constants  $k_i$  deduced here for radiation (other possibilities include thermal gravity waves, e.g. that which is predicted to be propagated in massive body collisions and other energy interactions arising from the independent forces predicted in particle theory).

Some other important considerations not developed here are the possible dependence of the mentioned fundamental constants on geometry and magnitude of the system.

## ACKNOWLEDGMENTS

I thank the AAAS Pacific Division organizers, in particular Daniel P. Sheehan (Physics Dept., U.S.D.) for drawing attention and inviting me to the 92<sup>nd</sup> Annual Meeting in San Diego. University of Malaya conference grant allocations from AFR Cluster and Human Resources Division were utilized for the visit. The work was prepared with assistance from grants FRGS FP084/2010A (Malaysian Government) and UMRG RG077/09AFR (U.M.).

## REFERENCES

1. C. G. Jesudason, *Malaysian J. Sci.* **14**, 61–79 (1992).
2. A. B. Bell, and D. Bell, *Found. Phys.* **9**, 472–476 (1979).
3. T. Boyer, *Phys. Rev.* **182**, 1374–1383 (1969).
4. T. H. Boyer, *Phys. Rev.* **186**, 1304–1318 (1969).
5. H. Callender, *Phil. Mag S.6* **26**, 787–791 (1913).
6. D. Cole, *Phys. Rev. A* **42**, 1847–1862. (1990).
7. D. Cole, *Phys. Rev. A* **42**, 7006–7024 (1990).
8. J. Jeans, *Phil. Mag.* **20**, 943–954 (1910).
9. O. Theimer, *Phys. Rev. D* **4**, 1597–1600 (1971).
10. O. Theimer, and P. Peterson, *Phys. Rev. D* **10**, 3962–3971 (1974).
11. J. Thomson, *Phil. Mag.* **26**, 792–799 (1913).
12. S. B. McLaren, *Phil. Mag S.6* **21**, 15–26 (1911).
13. M. Wax, *Selected Papers on Noise and Stochastic Processes*, Dover Publications, New York, USA, 1954.
14. Y. P. Terletsii, *Statistical Physics*, North-Holland Publishing Company, Amsterdam, Netherlands, 1971, transl. by Nanny Froman.
15. M. Planck, *The Theory of Heat Radiation*, Dover Publication, New York, USA, 1959.
16. F. Irons, *Can. J. Phys.* **83**, 617–628 (2005).
17. A. Hermann, *The Genesis of Quantum Theory*, MIT Press, Massachusetts, USA, 1971, cloth bound edn., planck, M. (1931). Letter to R.W. Wood, transl. by Hermann, A.
18. C. G. Jesudason, *J. Math. Chem.* **42**, 893–908 (2007).
19. R. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, vol. I, Addison-Wesley Publishing Company, 1965.
20. F. Reif, *Fundamentals of statistical and thermal physics*, McGraw-Hill Book Company, New York, USA, 1965.
21. T. Taylor, *Mechanics: Classical and Quantum*, Pergamon Press, Oxford and New York, 1976.
22. C. G. Jesudason, *Indian J. Phys.* **71B**, 661–683 (1997).
23. C. G. Jesudason, *Indian J. Phys.* **72B**, 19–33 (1998).
24. J. Holman, *Heat Transfer*, McGraw-Hill, New York, 1981, 5th edn.
25. Model P3300/1/2, manufactured by G. Cussons Ltd., 102 Great Clowes Street, Manchester H79RH, United Kingdom, complete with full specifications and instructions and manual for operation (1984).



26. J. R. Reitz, F. J. Milford, and R. W. Christy, *Foundations of Electromagnetic Theory*, Foundations of Electromagnetic Theory, Addison-Wesley, Reading, 1980.
27. M. F. Modest, *Radiative Heat Transfer*, McGraw-Hill, New York, 1993.
28. J. A. Wiebelt, *Engineering Radiation Heat Transfer*, Holt, Rinehart and Winston, New York, 1965.
29. J. M. Blakely, editor, *Surface Physics of Materials*, vol. 1, Academic, New York, 1975.
30. W. Duffin, *Advanced Electricity and Magnetism*, McGraw-Hill Publishing Company, New York (U.S.A.), 1968.
31. D. McQuarrie, *Statistical Mechanics*, Harper and Row, New York, 1976.
32. S. Benofy, and P. Quay S.J., "Fourier's Inequality as a Principle of Thermodynamics, with Applications to Magnetothermoelectric Effects," in *Physics as Natural Philosophy*, M.I.T. Press, Cambridge, Massachusetts, 1982, pp. 7-24.
33. C. G. Jesudason, "Studies in Thermodynamics," in **Ph.D Thesis**, University of Georgia, Athens, GA30602, U.S.A., 1986.
34. K. Khoury, and A. Neveu, *Int. J. Heat Mass Transfer* **32**, 213-226 (1989).
35. C. G. Jesudason, *Ind. J. Pure Appl. Phys.* **29**, 88-101 (1991).
36. C. G. Jesudason, *Ind. J. Pure Appl. Phys.* **29**, 163-182 (1991).